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PROCESS OF MAKING ORGANIC ESTERS OF CELLULOSE.

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This invention relates to processes of making organic esters of cellulose. One object of our invention is to provide an inexpensive and simple process in which we can utilize satisfactorily forms of cellulose which have proven difficult to esterify. Another object is to provide a process in which the cellulosic material is brought into such a condition that it will rapidly and uniformly esterify in the known reaction mixtures, such as those cutomarily employed for making cellulose acetate, for example. Still another object is to pretreat the cellulosic material before esterification in a mercerizing bath and then provide an auxiliary pretreatment which will conserve the good effects of the mercerization and yet avoid the resistance to esterification, which ordinarily follows the mercerization process. A further object is to provide a process in which the cellulosic material is especially prepared for esterification and may be dried and stored before esterification, without impairing its good qualities. A still further object is to provide a process of making the esters in which neither the pretreating nor the esterification causes any serious molecular degradation, as is evidenced by the qualities of films made therefrom. Other objects will hereinafter appear.

It has been generally customary to make cellulosic organic esters, especially cellulose acetate for the manufacture of films, from purified cotton of good grade and length. Clearly it is desirable to be able to utilize cheaper sources of cellulose, such as cotton linters, cotton dust, wood pulp, such as bleached sulfite pulp, soda pulp, etc. Furthermore, when utilizing cotton fibers of good grade, different batches often behave differently toward the esterification baths. Some of them require longer times for carrying out the reaction, and others show an unexpected tendency to leave incompletely esterified fiber particles in the reaction mixture. It is, therefore, desirable to find a way to minimize these peculiarities.

We have found that the less expensive, but more resistant, sources of cellulose may be used, and more uniform results may be obtained when employing the high grade celluloses, if the fibers are given a mercerizing pretreatment and dehydrated by means of a substantially anhydrous neutral organic liquid, preferably one that is volatile. The word "neutral" is used as meaning that the organic liquid is neither acid nor alkaline. In this way the emercerized fibers are never dried in the presence of water, but the organic liquid removes the water, and then the fibers can be dried, or utilized in the esterification bath while still containing some of the anhydrous liquid.

While we do not wish to be restricted to any particular theory, since the advantages of our process may be obtained irrespective of theoretical considerations, nevertheless we believe that our process owes much of its efficacy to the condition which it brings about in the surfaces of the cellulose fibers. When such fibers are mercerized, and the alkali washed out with water, and then the water driven off from them by an ordinary slow-drying method in the air, they become undesirably resistant to esterification. We believe that this is due to the formation of a hard, horny surface on the fibers which does not react readily with the esterification agents, the latter being unable to react with the inner parts of the fibers, while this tough cuticle remains. We further believe that our dehydrating of the washed mercerized fibers by means of inert organic anhydrous liquids prevents the formation of this hardened and unreactive outer surface on the fibers. Whether the fibers be then dried by evaporating off the organic liquid, or are stirred into the esterification mixture with some of the liquid still clinging to them, their surface remains in a soft and reactive condition which permits the esterification agents to react quickly with the surfaces of the fibers and then quickly with the interior portions thereof.

We shall now give several examples of our invention, but it will be understood that it is not limited to the details thus set forth, except as indicated in the appended claims. The cellulosic material, preferably in the fibrous form, is treated with a mercerizing

bath of the usual type, such as an aqueous solution of sodium hydroxid of 10% to 40% strength. While raised temperatures may be employed to hasten the mercerization, we find it ordinarily most convenient to work at room temperature. A bath consisting of and 18% solution of caustic soda in water works well. So long as a useful mercerization of the fibers is obtained, and the latter are not degraded, the time of the mercerizing is relatively unimportant. Using said 18% solution, we have obtained satisfactory results after one day's treatment at room temperature, but no harm has appeared after three days' treatment in such solution, and the time could obviously be prolonged without ill effect. Two days is a good average period. Caustic potash can be similarly used.

After the mercerization, the cellulosic material is washed with water, preferably at room temperature, or the temperature of the ordinary supply of water, which may be slightly below room temperature in the winter, or slightly above it in the summer. The fibers are thus rendered free from detectable quantities of alkali. Warm water can be used but is not necessary.

After this washing step, the excess of water is removed from the cellulosic material by pressure, say in a centrifuge, or better, in a hydraulic press. But care is taken that the fibers are not allowed to dry while they are still wet with the wash water.

The fibers are then dehydrated by means of a substantially neutral organic anhydrous liquid. Ethyl alcohol is a useful dehydrating agent, and may be employed to remove the water from the mercerized and washed fibers in practically the same way that it is often used for removing water from nitrocellulose fibers which have been previously washed in water. Methyl, propyl, butyl and amyl alcohols can also be used, but the higher boiling members of this group offer no marked advantages and are more expensive. Acetone has been found to be excellent as a dehydrating liquid, and ether, either mixed with ethyl or methyl alcohol, or applied after methyl or ethyl alcohol, has also been very effective in dehydrating the fibers and leaving them with their surfaces in the best condition for the subsequent esterification.

The lower members of the benzene series of hydrocarbons, such as benzol, toluol and xylol are also effective in this respect, benzol being preferred. When the latter is employed, the mercerized fibers carrying the residue of wash water are immersed in the benzol and kept below the surface of it during the treatment. The bath containing the fibers is then brought to its boiling point, which is less than that of benzol, owing to the formation of an azeotropic mixture of the latter with water. Thus the water is carried away by the distillation and the mercerized cellulose fibers remain wetted only with benzol and substantially free from water. Of course, the benzol which distills off with the water may be condensed and recovered for further use in the process.

After the cellulosic material is dehydrated, it may be freed from the dehydrating agent by evaporation, the vapors of the dehydrating liquid, such as alcohol, acetone, benzol etc., being condensed and thus recovered for future use. Or the cellulosic material may enter an esterifying bath with the dehydrating agent still in it. As a rule, it is slightly more convenient to evaporate off and recover the dehydrating liquid. Then the mercerized cellulosic material may be stored and kept indefinitely, until it is esterified, the surfaces of the fibers remaining in their reactive condition.

When the mercerized cellulosic fibers have been dehydrated with benzol, it may be economical to introduce them, while still wet with benzol, into an esterifying bath of the type in which there is present enough benzol, or other non-solvent to produce cellulose esters in the form of fibers. Of course, the benzol could be evaporated off before the films enter the bath, but that is an extra operation.

Our mercerized and dehydrated cellulosic material may be esterified in any of the usual cellulose esterifying baths in which organic acid anhydrids are employed. Since cellulose acetate is at present the most widely used of the organic esters of cellulose, we shall give examples of the many ecetylating baths which can be used, but it will be understoood that the known baths for forming cellulose propionates, butyrates, stearates and various mixed esters, such as aceto stearates, may be employed with equal facility. Our pretreatment brings the fibers into especially good condition for all of these baths.

In one illustrative embodiment of our invention, long fiber surgical cotton, properly cleaned, is mercerized in an 18% aqueous caustic soda solution at room temperature for one day and then washed with water at room temperature, being finally dehydrated with methyl alcohol, followed by ether. After dehydration the ether is evaporated and 5 parts by weight of the fibers stirred into a bath comprising 25 parts of acetic acid, 20 parts of acetic anhydrid, 20 parts of chloracetic acid, .1 part of magnesium perchlorate, and the reaction mixture kept at 60° to 65° C. until it becomes homogeneous and the fibers have all substantially dissolved. This is ordinarily reached in about three and one-half hours.

This is much less than the time required to acetylate the same long-fibered surgical

cotton after the same mercerizing treatment where no dehydrating step has taken place, but the washed mercerized fibers have been heated at 40° C. to drive off the water. Such air-dried mercerized fibers, when immersed in the above acetylating bath, are in such a highly resistant condition that they are only partially acetylated even after eight hours, numerous pieces of fiber being still visible in the reaction mixture. In fact, they require longer for acetylation than do the plain untreated long-fibered cotton. Our treatment brings about the acetylation in the shortest time of all and with a greater smoothness of reaction.

In another example of our invention, 10 parts by weight of mercerized and washed cellulose fibers are soaked in a 10% solution of magnesium perchlorate and pressed until the weight of the residue is 30 parts. This is then dehydrated by immersing in benzol and distilling as hereinabove described. The 10 parts of dehydrated fibers will thus be thoroughly associated with 2 parts by weight of magnesium perchlorate and the remaining anhydrous benzol, say 15 parts of the latter. This mixture is then added to a bath of 50 parts by weight of acetic anhydrid and 160 parts by weight of carbon tetrachlorid. In place of the latter any suitable diluent may be substituted,—say 90 90 parts by weight of benzol or toluol. The thoroughly mixed reaction mass thus obtained is kept at 50 to 55° C. until a sample shows that acetylation is complete. This may take several days. The fibers do not disappear during the reaction. They are separated from the other ingredients of the reaction mass in the usual way.

Our mercerized and dehydrated fibers may likewise be used to advantage in any of the esterification processes disclosed in our copending applications, Serial Nos. 179,176 and 179,177, filed March 28, 1928, entitled "Processes of making organic esters of cellulose containing acyl groups having more than two carbon atoms" and "Process of making cellulose esters of organic acids." They are very satisfactory in forming the esters of the fatty acids by the steps there disclosed.

In the above examples, in place of the long fiber surgical cotton, we can use less expensive materials, such as cotton linters, cotton dust, wood pulp, such as bleached sulfite pulp, soda pulp, and reverted cellulose, such as rayon fibers from the viscose or cuprammonium processes, these being substituted weight for weight in the above examples.

It is also noted that when mercerized cellulosic fibers have been dehydrated and dried by our treatment, their surfaces are in an especially susceptible condition toward the ordinary dyes used on cellulose fabrics, taking the color much more deeply than mercerized fibers which have been directly dried.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The process of making organic esters of cellulose which comprises mercerizing cellulosic material with an aqueous alkaline bath, dehydrating it with a substantially anhydrous neutral organic liquid, and thereafter subjecting the mercerized and dehydrated cellulosic material to the action of an esterifying agent.

2. The process of making organic esters of cellulose which comprises mercerizing the cellulosic material in an aqueous alkaline bath, washing out the alkali with water, removing the water with a substantially anhydrous neutral volatile organic liquid, and thereafter esterifying the mercerized dehydrated cellulosic material with an esterifying bath comprising a fatty acid anhydrid.

3. The process of making organic esters of cellulose which comprises mercerizing the cellulosic material in an aqueous bath having an alkalinity corresponding to from 10 to 40% of NaOH, washing out the alkali with water, removing the water with a substantially anhydrous and neutral organic liquid which is a nonsolvent of the ester to be produced, and thereafter treating the mercerized and dehydrated cellulosic material in an esterifying bath containing a fatty acid anhydrid.

4. The process of making organic esters of cellulose which comprises mercerizing the cellulosic material with an aqueous alkaline bath, washing out the alkali from the material with water, removing the water from the material with a substantially anhydrous neutral volatile organic liquid, evaporating said organic liquid from said material, and thereafter treating said mercerized dehydrated and dried cellulosic material with an organic esterifying agent.

5. The process of making cellulose acetate which comprises mercerizing cellulose, in a form which is resistant to esterification by acetic anhydrid, in an aqueous alkaline bath having an alkalinity corresponding to from 10 to 40% of NaOH, washing out the alkali from said material with water, removing the water from the material with a substantially anhydrous neutral volatile organic liquid, and thereafter acetylating the mercerized, washed and dehydrated cellulose in an acetylating bath containing acetic anhydrid.

6. The process of making cellulose acetate which comprises mercerizing cellulose, in a form resistant to esterification by acetic anhydrid, in an aqueous alkaline bath having an alkalinity corresponding to from 10 to 40% NaOH, at room temperature, washing out the alkali from the cellulose with water,

removing the water from said cellulose with benzol, and thereafter acetylating said mercerized, washed and dehydrated cellulose in an acetylating bath containing acetic anhydrid.

7. In the process of preparing cellulose for subsequent treatment in chemical baths, the steps of mercerizing the raw cellulose with an aqueous alkaline bath, removing the alkali, and dehydrating the mercerized cellulose with a substantially anhydrous neutral organic liquid, whereby drying off water from the mercerized cellulose in air is avoided.

Signed at Rochester, New York this 18th day of April, 1927.

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